FUNCTIONAL GROUP ANALYSIS OF COAL AND COAL PRODUCTS BY
X-RAY PHOTOELECTRON SPECTROSCOPY

David L. Perry and Alan Grint

BP Research Centre, Sunbury on Thames, Middlesex, TW16 7LN, UK.

The functional group composition of coal and coal products has a determining
influence on their properties, affecting efficiency of utilisation. Also, it
is well established that the oxidation which occurs when fresh coal is exposed to
the atmosphere causes a marked deterioration in coal quality, affecting properties
such as heating value, floatability and coking potential. The application of
techniques such as Fourier transform infra-red (FTIR) spectroscopy and magic angle
spinning nuclear magnetic resonance (NMR) spectroscopy has led, in recent years,
to significant improvements in our understanding of the nature of carbon-oxygen
functional groups in coal and the changes induced by different coal treatments.

In a number of technologies such as polymers and carbon fibres, where there is a
similar interest in the nature of organic functional groups and their effect on
material performance, the technique of x-ray photoelectron spectroscopy (XPS),
also known as electron spectroscopy for chemical analysis (ESCA), has been
applied successfully to a wide range of problems. However XPS is a technique
which is little used in coal science. Since it has high surface sensitivity and
the specific surface properties of coals play an important role in a number of
coal technologies, e.g. floatation and agglomeration, it is perhaps surprising
that XPS is not used more extensively. The reasons for this may lie in some of
the discouraging references in the literature. For example early work by Frost
et al (1) found no relationship between oxygen concentrations determined by XPS
and the bulk analysis of a series of float-sink fractions. More recently Huffmann
et al (2) observed that oxidation of bituminous coals for up to 383 days at 50°C
in air completely destroyed Geiseler fluidity but neither XPS nor DRIFT (Diffuse
Reflectance FTIR) spectroscopy could detect any parallel changes in the functional
group composition of the coal.

This paper describes the application of XPS to coal, coal reactions and coal
products. The aim is to present a critical evaluation in the context of other
techniques which are applied to coal.

THE XPS TECHNIQUE

X-ray photoelectron spectroscopy is fully described in a number of reviews
e.g. (3). It involves measurement of the kinetic energies of core and valence
electrons photoemitted from a (usually) solid sample when irradiated by soft
x-rays (normally Mg or AlKα). The experiment is carried out within a vacuum
system (pressure$<$ 1 x 10^{-5} Pa). Since core electrons have characteristic
binding energies, the photoelectron spectrum provides an analysis for all elements
except hydrogen and helium. The electrons detected are emitted only from the
outermost 3-4nm of the solid; the analysis is therefore of a few atomic layers at
the exposed surface. Different oxidation states or functional groups give rise
to chemical shifts in the characteristic binding energies of contributing
elements. For carbon (1s) spectra in coal the chemical shifts show themselves
as a peak broadened to higher binding energy by the presence of different
carbon-oxygen functional groups. The broadened spectra can be resolved into
components corresponding to the functional group types which are assumed to
contribute to the peak envelope. An example for a lignite C(1s) spectrum is
given in Figure 1. The separation of the components depends upon the carbon
oxidation state as follows: State CI (hydrocarbon) at 285eV, CII (singly bonded
carbon-oxygen i.e. hydroxyl or ether) at 286.6eV, CIII (carbonyl) at 288eV and CIV
(carboxyl, acid or ester) at 289.2eV (4). The positions of these components

relative to the principle hydrocarbon component are well established from model
compound studies both reported in the literature and confirmed by the present
authors.

Peak synthesis routines however do not provide a unique solution. Their accuracy
is dependent on the suitability of transferring chemical shifts from simple model
compounds to a more complex material. Uncertainty in peak synthesis arises from a
lack of definition of the fundamental spectral lineshape for each component.
Standard routines use Gaussian or Gauss/Lorentzian mixtures. Because of the
aromatic nature of coal the fundamental lineshape is thought to be asymmetric but
the precise shape has yet to be determined (5). The effect of using symmetric
components rather than the correct lineshape, may be to exaggerate the
concentration of carbon attached to oxygen, particularly in the CII state.

The most important features of XPS when compared with other instrumental techniques
are:-

1) High surface sensitivity (information about the bulk of coal particles can be
obtained by grinding to a smaller particle size).

2) Although different carbon-oxygen functional groups are not well-resolved, the
constant sensitivity of XPS to the element rather than the functional group, means
that functional group analysis is quantitative within the accuracy of the peak
synthesis routine.

3) Quantitative functional group and elemental analysis in the same experiment
allows validation of interpretation e.g. the changes in the carbon-oxygen
functional groups can, in principle, be correlated with the oxygen concentration
changes.

4) Functional group analysis can be applied to other elements of interest e.g.
sulphur and nitrogen.

SURFACE COMPOSITION OF COALS

An example of the difference which can exist between the surface and bulk composition
of coal particles, and hence the importance of appropriate sample preparation when
using XPS, is illustrated in Table 1. The bituminous coal fines (particle size
$500-38\mu$) show very different surface compositions when examined as received,
compared with the same material after grinding under heptane to $< 5\mu$. The coal is
clearly very heavily surface oxidised, having twice as much organic oxygen as the
heptane ground exposed surfaces. Such differences between surface and bulk oxygen

TABLE 1: SURFACE ANALYSIS OF BITUMINOUS COAL BY XPS (% ATOM RATIOS)

Element	As Received ($500 - 38\mu$)	Heptane Ground ($< 5\mu$)
C	100	100
O Total	52	29
O Mineral	28	17
*O Organic	24	12
Si	10.0	6.3
Al	5.0	3.0

* Organic oxygen cannot be resolved from mineral oxygen. It is calculated by
subtraction of mineral oxygen (calculated from Si and Al concentrations
assuming stoichiometry SiO_2 and Al_2O_3) from the measured total oxygen
concentration.

and the lack of correction for mineral oxygen, probably accounts for the poor
XPS/bulk correlations obtained by previous authors (1). When a rank range of
coals are prepared by grinding under heptane or under nitrogen just prior to
analysis, a good correlation can be obtained between surface organic oxygen and
bulk analysis (4). For a series of preasphaltenes the correlation for oxygen,
sulphur and nitrogen is similarly good (6).

The distribution of oxygen between surface and bulk following weathering or
deliberate oxidation is of particular significance for those coal technologies,
such as froth flotation and oil agglomeration where surface properties govern the
efficiency of the process.

THERMAL OXIDATION STUDIES

There has been considerable interest in recent years about the nature of
carbon-oxygen functional groups introduced by thermal oxidation. FTIR studies
have generally concluded that incorporation of oxygen as carbonyl or carboxyl
groups is the dominant effect of oxidation (7,8).

We have previously shown (9) in XPS studies of the inhibition of Geiseler fluidity
by oxidation, that exposure to air at 100°C causes predominantly a surface
oxidation to occur and that oxygen is incorporated almost entirely as alcoholic or
phenolic OH groups. This study has been extended by looking at the oxidation of
Pittsburgh coal ($<450\mu$) in flowing air at three temperatures; 100, 150 and 200°C.
Plots of the oxygen uptake by the surface and the bulk (revealed by heptane
grinding after oxidation) are shown in Figure 2. A common feature of these data
is the difference between the surface and bulk concentration of oxygen as the coal
particle is oxidised. The concentrations diverge with time and the surface to
bulk ratio is greater at the higher temperatures. At 100°C very little bulk
oxidation of the coal is observed. It is clear that oxidation of these coal
particles is diffusion limited at all three temperatures. This result appears to
contradict the conclusions drawn by Chien et al (10) who concluded from
FTIR-photoacoustic studies that oxidation of Illinois No 6 coal at 150°C was not
diffusion limited. However this could be explained by differences in coal
porosity, the Pittsburgh coal being mainly microporous.

Figure 3 shows the changes which occur in the carbon (1s) spectra on oxidation at
200°C. Evidence of carbon-oxygen groups formed is clearly visible on the high
binding energy side of the peak; these being much more evident on the surface than
in the bulk. The results of curve fitting the spectra are in Table 2. At all
temperatures the formation of singly bonded species ie ether or OH groups, referred
to as state CII in the peak synthesis, dominates in the early stages of oxidation.
Even at 200°C, where carboxyl group formation is clearly favoured on the surface,

TABLE 2:   CARBON (1s) PEAK SYNTHESIS OF OXIDISED PITTSBURGH COAL
(ATOM % TOTAL CARBON)

| | Fresh Coal | Oxidised 100°C 48 hours | | Oxidised 200°C 48 hours | |
	Surface & Bulk	Surface	Bulk	Surface	Bulk
O organic	8.7	11.0	10.2	38.6	20.0
CI	80.0	78.8	79.9	61.0	66.9
CII	12.3	12.7	12.0	20.0	17.0
CIII	2.0	2.4	2.0	5.3	2.8
CIV	1.6	1.6	1.5	7.7	4.7

the increase in carboxyl oxygen (2 x CIV) does not exceed greatly the increase in CII oxygen up to 48 hours of oxidation. This agrees with our previous results on temperature programmed oxidation of a bituminous coal (4), later confirmed by FTIR, that carboxyl group formation only became dominant above 200°C. The results from the most heavily oxidised coal indicate some limitations in the present methods of carbon (1s) peak synthesis since there is a lack of correlation between the oxygen increase and the carbon functional group analysis.

The results of our XPS study are in disagreement with previous FTIR studies. Painter et al (7) have reported that there is no evidence for OH formation on oxidation of a caking coal. In a subsequent study, on a different bituminous coal, Rhoads et al (8) report an initial increase in phenolic OH after ten hours at 140°C, though over 280 hours there is a decrease to a level below that of the fresh coal. In both cases the spectra are dominated by carbonyl and carboxyl peaks. NMR studies (11) of the same oxidised coal, however, showed no evidence for carbonyl or carboxyl group formation; changes involving oxygen incorporation were restricted to phenol formation up to 16 days at 140°C followed by condensation to form ethers at longer oxidation times.

The apparent disagreement between results from different techniques can be explained in general terms by the use of different coals, different oxidation conditions and the high sensitivity of FTIR spectroscopy to C=O groups. To resolve these differences there is a clear need to apply XPS, NMR and FTIR to an examination of the same samples of oxidised coal. The use of chemical derivatisation is likely to be an aid to spectral interpretation. An example of this combined approach applied to some preasphalteres will be described in a later section.

COAL OXIDATION BY WEATHERING

The laboratory simulation of the effects of weathering on the chemistry of coal is usually carried out by thermal oxidation i.e. exposure of beds of coal to air at an elevated temperature. Unlike weathering studies of polymer films and coatings, the influence of photoinduced reactions through exposure to light are not generally considered. This is probably realistic for simulation of weathering on stockpiled coal where the surface area of coal exposed to light is negligible. The effect of light does however have potential consequences for the storage of small quantities of coal for laboratory experiments, particularly when surface properties are being investigated.

The effect of daylight on the oxygen content of exposed coal surfaces has been tested by taking a sample of Pittsburgh No 8 coal, ground under heptane, and mounted on a sample probe for analysis by XPS. Before analysis the sample was exposed to a north facing window for a period of five days at an ambient temperature of 18°C. The changes induced by this exposure to diffuse sunlight are presented in Table 3. The degree of surface oxidation is substantial; oxygen is incorporated into the surface at a level not reached after 24 hours oxidation at 150°C. The peak fitting shows significant increases in all oxygen groups, with substantial formation of OH and carboxyl groups.

TABLE 3: CARBON (1s) PEAK SYNTHESIS OF 5 PITTSBURGH COAL
EXPOSED TO DAYLIGHT FOR FIVE DAYS (ATOM % TOTAL CARBON)

	Fresh	Exposed
0 Organic	8.7	23.3
CI	80.0	72.6
CII	12.3	14.9
CIII	2.0	3.5
CIV	1.6	5.0

FUNCTIONAL GROUP ANALYSIS OF PREASPHALTENES BY DERIVATISATION

Derivatisation of OH groups by acetylation is a widely used technique to enhance the sensitivity and resolution of infra-red spectroscopy. It can also be used in XPS to enable the discrimination of OH from ethers in the CII state by conversion of OH groups to esters (CIV). We have applied this technique to preasphaltenes in the first instance since the reaction can be carried out in solution. This avoids problems of selective extraction when solid coals are treated with organic solvents.

Preasphaltenes (THF soluble, toluene insoluble) obtained from a bituminous coal in tetralin and hydrogen were acetylated at 40°C for 24 hours using pyridine and acetic anhydride. The resultant solution was rotary evaporated to dryness using toluene and dried in a vacuum oven. Table 4 shows the data obtained from peak synthesis of the carbon (1s) envelope, revealing the nature of the surface groups of an acetylated and unacetylated preasphaltene. The increase in the CIV carbon state (3.6%) of the derivatised sample shows that acetylation has occurred. This is in reasonable agreement with the observed increase in organic oxygen (4.7 O/C atomic %). As expected no increase was observed in the CII carbon state (singly bonded carbon-oxygen), though a reduction in carbonyl was a reproducible feature.

TABLE 4: CARBON (1s) PEAK SYNTHESIS OF ACETYLATED PREASPHALTENE
(Atom % Total Carbon)

	Preasphaltene	Acetylated Preasphaltene
Oxygen	10.8	15.5
CI	77.9	72.3
CII	14.4	14.9
CIII	1.9	1.1
CIV	1.5	5.1

In order to evaluate the XPS data obtained from this experiment a series of preasphaltenes were analysed and quantified using four techniques in parallel: (XPS, FTIR (12) and ^{13}C NMR) on acetylated preasphaltenes, plus enthalpimetric titrations (13) on the original preasphaltenes. Table 5 reports the results obtained. All techniques are in reasonable agreement validating the use of XPS to give a quantitative assessment of the hydroxyl content in carbonaceous materials. Generally the enthalpimetric technique gives the highest value for oxygen as hydroxyl whereas FTIR and XPS gave similar but lower values. The good agreement between the different techniques suggests that combined FTIR, NMR and XPS studies of acetylated coals after oxidation might resolve some of the existing differences in the literature.

TABLE 5: OXYGEN AS OH IN PREASPHALTENES MEASURED BY NMR, FTIR,
XPS AND ENTHALPIMETRIC TITRATION

Sample	Analysis	Oxygen as OH Relative to C = 100			
		NMR	FTIR	Titration	XPS
1	$C_{100} H_{87} O_9$	5	4.5	5.4	4.0
2	$C_{100} H_{83} O_8$	3	3.8	5.0	3.8
3	$C_{100} H_{76} O_5$	3	3.0	3.9	3.1

NITROGEN GROUPS IN COAL

Although the role of nitrogen in coal is not thought to be of direct importance in determining coal properties, there is interest in determining the fate of nitrogen

during combustion or liquefaction. This requires identification of the nitrogen functional group type at each processing stage. Previous work had shown that the nitrogen (1s) peak in coal could be resolved into two components corresponding to pyrrole and pyridine type groups (14). We have confirmed this model and shown that over the rank range of coals the preparation of each component remain approximately constant at around 2:1 pyrrole to pyridine. Carbonisation increases the proportion of pyridine groups.

Examination of some chemically separated asphaltene fractions has validated the analysis of the N(1s) peak by showing that in basic fractions the pyridine type groups are the major component (15). Examples of the spectra are shown in Figure 4. The asphaltene has a similar nitrogen group distribution as the parent coal.

Assignment of the pyridine component has been further supported by derivatisation experiments to form the pyridinium ion. This species can be readily distinguished by XPS (15).

CONCLUSIONS

These studies have demonstrated that XPS has specific and unique advantages for the examination of coal surfaces. Determination of the carbon-oxygen functional group chemistry at coal particle surfaces should enable a better fundamental understanding of many coal beneficiation and utilisation processes. However when proper consideration is given to sample preparation XPS can also contribute to improvements in our fundamental understanding of bulk coal chemistry. Developments are required to improve the accuracy of curve resolution methods, probably involving chemical derivatisation. Studies of Pittsburgh No 8 oxidation have revealed the distribution of oxygen and carbon-oxygen species between surface and bulk and have indicated the importance of OH group formation during oxidation. In several respects XPS can be seen to complement more conventional spectroscopies. This applies especially to sulphur and nitrogen functional group chemistry in which there is increasing interest due to environmental pressures. XPS is likely to be one of the more useful spectroscopic techniques for looking at these groups and their reactions during utilisation.

REFERENCES

(1)   Frost, D.C., Leeder, W.R. and Tapping, R.L., Fuel, 53 206, (1974).

(2)   Huffmann, G.P., Huggins, F.E., Dunmyre, G.R., Pignocco, A.J. and Lin, M.C., Fuel, 64, 89, (1985)

(3)   PRACTICAL SURFACE ANALYSIS BY AUGER AND X-RAY PHOTOELECTRON SPECTROSCOPY, edited by Briggs, D. and Seah, M.P., John Wiley, (1983).

(4)   Perry, D.L. and Grint, A., Fuel, 62, 1024, (1983).

(5)   Cheung, T.T.P., J. Appl. Phys. 55, 1388, (1984).

(6)   Perry, D.L. and Grint, A., Unpublished Work.

(7)   Painter, P.C., Coleman, M.M., Snyder, R.W., Mahajan, O., Komatsu, M. and Walker, P.L., Appl. Spectrosc. 35, 106, (1981).

(8)   Rhoads, C.A., Senftle, J.T., Coleman, M.M., Davis, A. and Painter, P.C.,
       Fuel, 62, 1387, (1983).

(9)   Grint, A. and Perry, D.L., Proceeding of 1985 International Conference
       on Coal Science, Sydney, Australia, 1985, p 879.

(10)   Chien, P.L, Markuszewski, R. and McClelland, J.F., ACS Division of Fuel
       Chemistry Preprints, 30 (1), 21 (1985).

(11)   Havens, J.R., Koenig, J.L., Kuehn, D., Rhoads, C.A., Davis, A. and
       Painter, P.C., Fuel, 62, 936, (1983).

(12)   Snyder, R.W., Painter, P.C., Havens, J.R. and Koenig, J.L., Appl,
       Spectrosc. 37, 497, (1983).

(13)   Vaughan, G.A. and Swithenbank, J.J., Analyst, 95, 890, (1970).

(14)   Jones, R.B., McCourt, C.B., and Swift, P., Proceedings of International
       Conference on Coal Science, Dusseldorf, 1981, p 657.

(15)   Bartle, K.D., Perry, D.L., and Wallace, S., Paper to be presented at
       First International Rolduc Symposium on Coal Science, The Netherlands
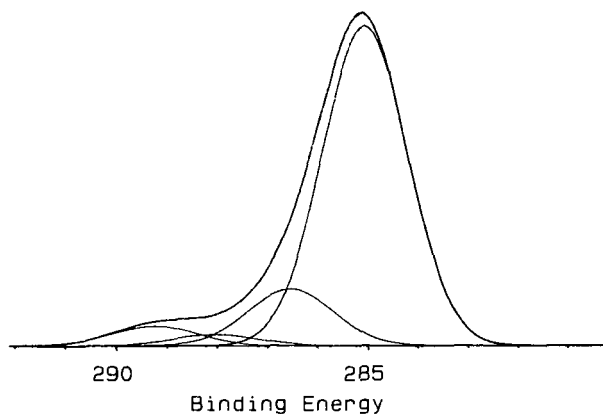   1986.

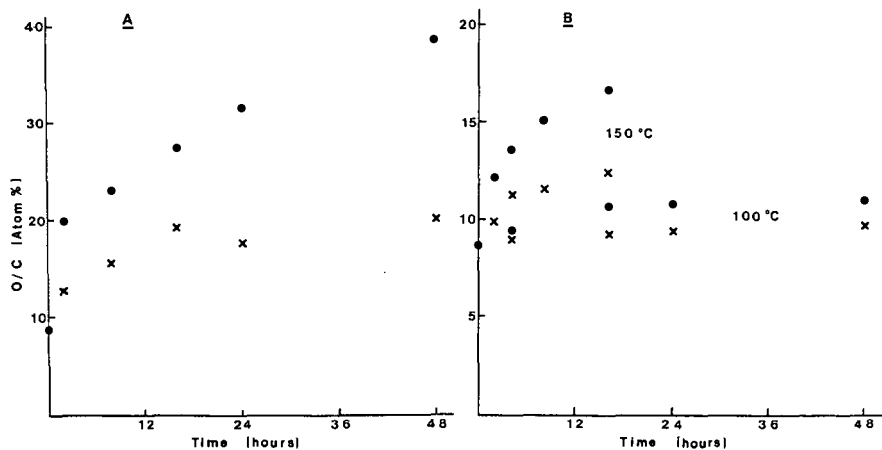FIG 1. EXAMPLE OF C(1s) PEAK SYNTHESIS FOR A LIGNITE

FIG 2. CHANGES IN ORGANIC OXYGEN CONCENTRATION FOR OXIDISED PITTSBURGH COAL: A-200°C, B-150 AND 100°C, ● - SURFACE, ✗ - BULK.
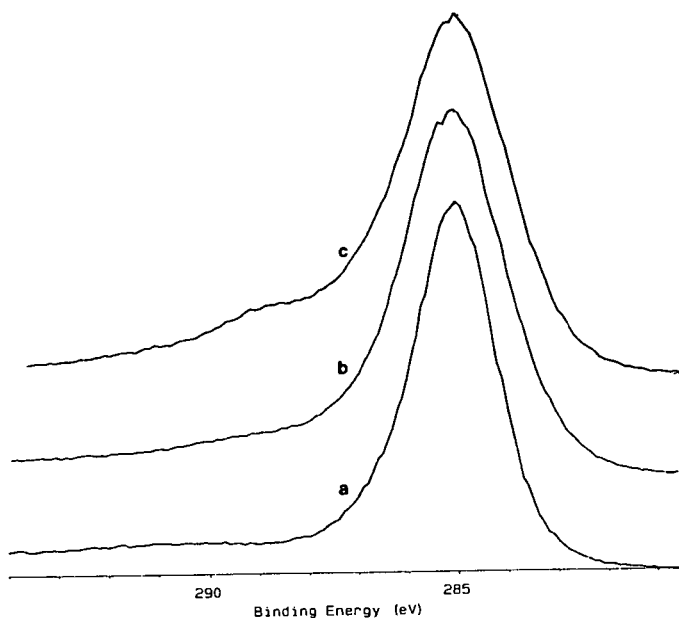
290   285

Binding Energy (eV)

FIG 3: COMPARISONS OF C(1s) SPECTRA OF PITTSBURGH COAL OXIDISED AT 200°C
a) INITIAL COAL, b) OXIDISED 48 HOURS – BULK, c) OXIDISED 48 HOURS – SURFACE .

402   400   398   402   400   398
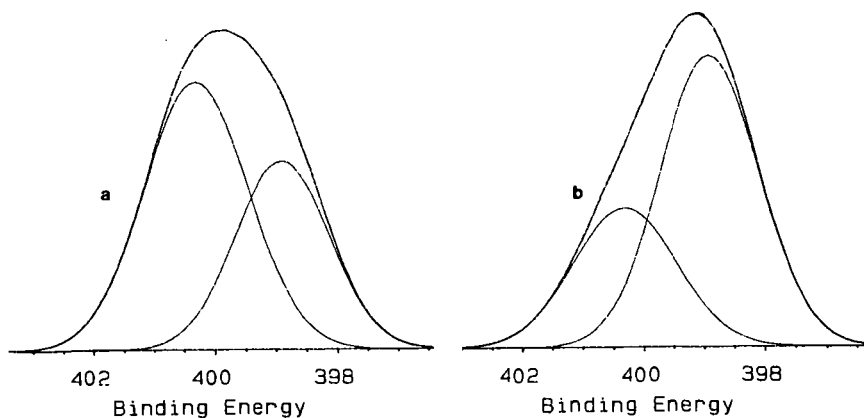
Binding Energy   Binding Energy

FIGURE 4: N(1s) SPECTRA OF a) ASPHALTENE, b) BASIC FRACTION OF ASPHALTENE (PYRIDINE
COMPONENT AT 398.8eV, PYRROLE COMPONENT AT 400.2eV).

115